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Impact of Biomass Burning emission on total peroxy nitrates: fire plume identification during the BORTAS campaign

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Abstract

The total peroxy nitrates (∑PNs) concentrations have been measured using a thermal dissociation laser induced fluorescence (TD-LIF) instrument during the BORTAS campaign, which focused on the impact of boreal biomass burning emissions on air quality in the Northern hemisphere. The strong correlation observed between the ∑PNs concentrations and those of the carbon monoxide (CO), a well-known pyrogenic tracer, suggests the possible use of the ∑PNs concentrations as marker of the biomass burning (BB) plumes. We applied both statistical and percentile methods to the ∑PNs concentrations, comparing the percentage of BB plume selected using these methods with the percentage evaluated applying the approaches usually used in literature. Moreover, adding the pressure threshold (~750 hPa) to ∑PNs, HCN and CO, as ancillary parameter, the BB plume identification is improved. An artificial recurrent neural network (ANN) model was adapted to simulate the concentrations of ∑PNs and the HCN including as input parameters ∑PNs, HCN, CO and atmospheric pressure, to verify the specific role of these input data to better identify BB plumes.

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1. Introduction

Biomass burning (BB) events are an important source of many trace gases and particles in the atmosphere [Crutzen et al., 1979; Crutzen and Andreae, 1990; Goode et al., 2000; Andreae and Merlet, 2001,]. The signature of BB emission in a plume detected far away from the fire is usually the increase of the atmospheric concentration of pyrogenic species including carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4) and a series of volatile organic compounds (VOCs), accompanied by elevated concentrations of peroxyacyl nitrate (PAN) [e.g., Goode et al., 2000; Cofer et al., 1998; Bertschi et al., 2004; Dibb et al., 2003; Lewis et al., 2007, Tereszchuk et al 2011].

In recent years, several studies have focused on boreal forest fires to quantify the influence of boreal fire emissions on the Earth-Atmosphere system and subsequent impact on the climate. Boreal forest fires (http://www.borealforest.org) affect mainly Siberia, Canada and Alaska and occur generally from May to October (Lavoué et al., 2000). In the past three decades occurrence of boreal forest fires and areas burned over Canada have both increased (Gillett et al., 2004; Rinsland et al., 2007; Marlon et al., 2008). The impact of boreal BB on atmospheric chemistry is triggered by the large emissions of CO, NO_x ($NO + NO_2$), nonmethane hydrocarbons (NMHC) and other NO_y species (Alvarado et al., 2010; Parrington et al., 2012): $NO_y = NO_x + \sum RONO_2 + \sum RO_2NO_2 + HNO_3 + HONO + 2N_2O_5 + NO_3$, where $RONO_2$ are total alkylnitrates (known also as $\sum$ANs), RO_2NO_2 are total peroxynitrates (known also as $\sum$PNs), HNO_3 is nitric acid, HONO is nitrous acid, N_2O_5 is dinitrogen pentoxide and NO_3 is nitrate radical. These species can influence the formation of O_3 in the Artic and at the mid latitudes: the role of boreal BB emissions on the O_3 concentration has been studied by several authors showing situations where O_3 concentrations increased and others where it was unaffected (e.g. Wofsy et al., 1992; Jacob et al., 1992; Mauzerall et al., 1996; Wotawa and Trainer, 2000; Val Martin et al., 2006; Real et al., 2007; Leung et al., 2007, Jaffe and Wigder, 2012; Parrington et al., 2012). The formation of NO_x oxidation products ($\sum$ANs, $\sum$PNs and HNO_3) plays a very important role in controlling the ozone budget as they inhibit local O_3 formation (Leung et al., 2007). Many investigations demonstrated the central role played by the peroxy acetyl nitrate (PAN), one of the most common PNs, in BB plume chemistry and, specifically, in the NO_x oxidation processes (Jacob et al., 1992; Hudman et al., 2007). Alvarado et al. (2010) demonstrated the rapid PAN formation occurring within 1-2 hours after the emissions by a BB plume: the 40% of the NO_x initially emitted by the fires is rapidly converted into PAN and the 20% into NO_3 (particles phase). In aged plumes, PAN can represent up to the 67% of the NO_y budget (Alvarado et al., 2010).

Analysis of chemistry of BB emissions starts with identifying a BB plume; however, previous studies have used multiple different approaches for the identification and classification of BB plumes. Many studies have recognized CO as a pyrogenic species (Crutzen et al., 1979; Andreae and Merlet, 2001;

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Lewis et al., 2013), but other chemical species, such as HCN and CH_3CN, have also been employed to identify a BB plume. In the assembly of the BORTAS data analysis, different procedures have been applied. Palmer et al. (2013) identified a threshold for each of these species that would separate air masses produced during boreal BB from background air masses; they defined a BB plume when the CO, hydrogen cyanide (HCN) and acetonitrile (CH_3CN) levels are higher than 148 ppb, 122 ppt and 150 ppt, respectively. These thresholds correspond to the 99th percentile (~mean±3σ) of the data for the species measured during the flight B625, in which there was not a significant correlation between the CO and the CH_3CN. In the context of the BORTAS campaign, Lewis et al. (2013) classified the air masses in three groups: 1) background if CO < 200 ppb; 2) BB plumes if the CO > 200 ppb with the presence of pyrogenic species such as furan or furfural; 3) anthropogenic plumes if CO > 200 ppb with the absence of furan or furfural. Le Breton et al (2013) observed a strong correlation between the HCN, CO and CH_3CN indicating the utilisation of HCN as a BB marker. They identified a BB plume using a standard deviation (σ) method applied to the 1 Hz HCN measurements: when the HCN concentrations were 6σ above the background for the flights in analysis, they flagged the air mass as a BB plume. The 6σ threshold was chosen since it produces the highest R^2 values for the correlation between the HCN and the CO. For other experiments different methods for the BB plumes identification have been suggested: 1) Holzinger et al. (2005) used a method similar to that used by Le Breton et al. (2013); their results highlighted a good correlation between acetonitrile (CH_3CN) and CO and they identified BB plumes by significant peaks in the CH_3CN volume mixing ratio (using a threshold of 3σ above the background level); 2) Vay et al. (2011) identified a plume when CO > 160 ppb (the median observed CO concentration at the surface), CH_3CN > 225 ppt (threshold characterized by an evident enhancement in CH_3CN mixing ratios) or HCN > 500 ppt (when the CH_3CN was not available); 3) Hornbrook et al. (2011) defined a plume by elevated fire tracers above the local background using thresholds of CH_3CN > 200 ppt, HCN > 400 ppt and CO > 175 ppb; 4) Tereszchuk et al. (2011) selected as BB plumes air masses when HCN > 350 ppt, assuming that background concentrations of HCN in the free troposphere range between 225 ppt and 250 ppt and, finally, 5) Alvarado et al. (2010) observed the enhancement of CO correlated with an enhancement in HCN and CH_3CN; they identified a plume as having a CO concentration at least 20 ppb above the background level.

An aircraft campaign was conducted in Nova Scotia (Canada) with the principle purpose of evaluating the BB emissions impact on tropospheric photochemistry in the Northern Hemisphere. This work is part of the BORTAS project (quantifying the impact of BOReal forest fires on Tropospheric oxidants over the Atlantic using Aircraft and Satellites). This project included a field campaign using a research aircraft (the FAAM BAe-146) conducted in July and August 2011 during the boreal forest

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fire season in Canada. Further details about this project can be found in Palmer et al. (2013) and at http://www.geos.ed.ac.uk/research/eochem/bortas/.

In our analysis of the BORTAS aircraft measurement data, we found a good correlation between the ∑PNs and CO, suggesting the potential of ∑PNs as pyrogenic tracer to discriminate the BB plumes. Therefore, in this work we propose two different methods to use the ∑PNs as BB tracer: a statistical approach using the 6σ threshold and the 99th percentile of the ∑PNs calculated for the B625 flight. We evaluated all of the methods described above to our dataset to compare the results of different methods to identify BB plumes. We show also that, in some cases, the introduction of meteorological parameters, which take into account of the air masses vertical position in the atmosphere, discriminates better the origin of the air masses and, then, helps to select more precisely a BB plume. Finally, in order to refine the method we adapted an artificial neural network model and we used it to simulate the ∑PNs and the HCN in two different procedures to BB plume identification: 1) using as inputs the CO, NO, CH_3CN; 2) adding to the inputs also the pressure.

2. Experimental

2.1 TD-LIF measurements: NO_2, ∑PNs, ∑ANs

A detailed description of the BORTAS experiment can be found in Palmer et al. (2013), along with a description of the FAAM BAe-146 instrumental payload. During BORTAS campaign (Canada, summer 2011), observations of NO_2, total ∑PNs, ∑ANs, on board the British FAAM BAe 146 research aircraft, were carried out using the TD-LIF (Thermal Dissociation – Laser Induced Fluorescence) instrument developed at the University of L'Aquila (Italy) (Dari-Salisburgo et al., 2009; Di Carlo et al., 2013). Briefly, this technique uses direct measurements of NO_2 molecules by Laser Induced Fluorescence (LIF), whereas ΣPNs, ΣANs and HNO_3 are thermally dissociated into NO_2 heating the air sample at 200°C, 400 °C and 550°C, respectively (Day et al., 2002; Di Carlo et al., 2013).

2.2 Ancillary measurements: O_3, CO, VOCs

Table 1 reports a number of the compounds measured on-board the BAe-146 aircraft during the BORTAS campaign, specifically those used in this analysis. The instrument used to measure O_3 was a commercial UV absorption system Model 49C (Thermo Environmental Corp.) (Wilson and Birks, 2006). CO was measured using the vacuum ultraviolet (VUV) resonance fluorescence technique. This type of CO instrument was applied to aircraft measurement by Gerbig et al. (1999). NO was measured using a single-channel chemiluminescence instrument manufactured by Air Quality Design, Inc.

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(Colorado, USA, http://www.airqualitydesign.com/) (Lee et al. 2009; Reidmiller et al. 2010). Concentrations of volatile organic compounds (VOCs) ranging from C5 to C12 were measured by an automatic gas chromatograph system equipped with a mass spectrometer GC-MS (Purvis et al. 2013). C2-C7 hydrocarbons and C2-C5 oxygenated volatile organic compounds (o-VOCs) including alcohols, aldehydes, ketones and ethers were obtained by the University of York (UK) using whole air sampling (WAS) coupled to an automatic gas chromatograph system equipped with a mass spectrometer and a flame ionization detector (GC-MS/FID) (Hopkins et al. 2003). Measurements of a suite of volatile organic compounds: CH_3CN, C_3H_6O, C_5H_8, MVK+MACR, C_4H_8O, C_6H_6, C_7H_8, $C_{10}H_{16}$ were made by proton transfer reaction mass spectrometry (PTR MS) (Murphy et al. 2010). Finally, a chemical ionisation mass spectrometer (CIMS) was used for measuring hydrogen cyanide (HCN) from biomass burning events (Le Breton et al., 2013).

Table 1. List of FAAM BAe-146 instrumental payload and observed compounds used in the analysis in this paper. A description of the FAAM BAe-146 instrumental payload, with accuracy and detection limit, is reported in Palmer et al. (2013).

Species	**Method**	**Reference**
CO	VUV resonance/fluorescence	Gerbig et al. (1999)
O_3	UV absorption	Wilson and Birks (2006)
NO_2 , ΣRO_2NO_2, $\Sigma RONO2$, NO_y	TD-LIF	Dari-Salisburgo et al. (2009); Di Carlo et al. (2013)
NO	AQD chemiluminescence	Lee et al. 2009; Reidmiller et al. 2010
C_5–C_{12} VOCs	GC-MS	Purvis et al. (2013)
C_2–C_7 NMHCs, acetone CH_3OH	WAS-GC	Hopkins et al. (2003)
HCN	CIMS	Le Breton et al. (2013)

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CH_3CN, C_3H_6O, C_5H_8, MVK+MACR, C_4H_8O, C_6H_6, C_7H_8, $C_{10}H_{16}$	PTR-MS	Murphy et al. (2010)

3. Plume identification

Figure 1 shows the time series of the species investigated in this paper (∑PNs, acetonitrile, HCN, CO and furfural) for one of the flights analysed (B623), illustrated as an example. The ∑PNs trends shows exactly the same structures present on CO and CH_3CN, with the exception of two plumes (in the temporal intervals of $(8.2 - 8.4) \times 10^4$ and $(8.6 - 8.8) \times 10^4$ seconds After Midnight (A.M.)) that are extensively analysed in the next sections. Moreover, the furfural shows similar trend for the first part of the flight; since CO, acetonitrile, HCN and Furfural are a known BB tracers (Lewis et al. 2013; Palmer et al. 2013; Le Breton et al., 2013), the significant correlation between the ∑PNs and those species suggests that the ∑PNs also originated at the same boreal biomass burning source and that it can be used as additional chemical species for the identification of the BB plumes.

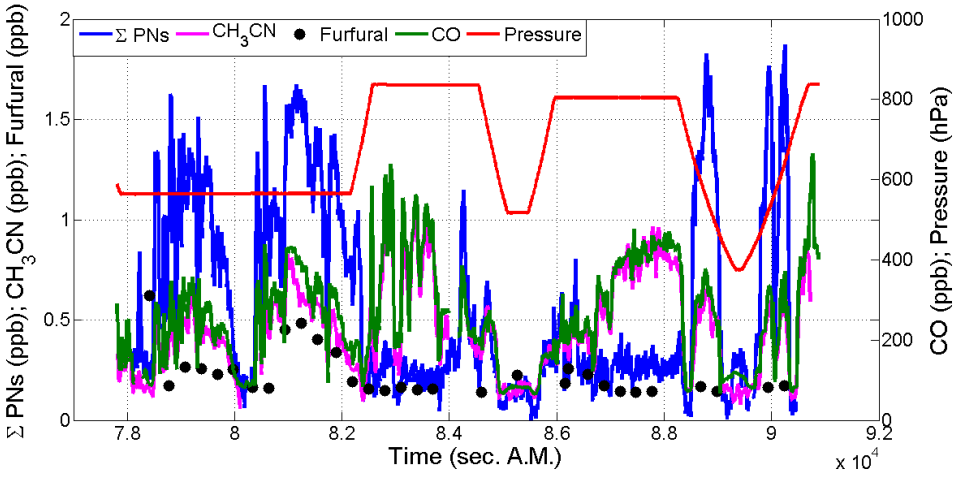

Figure 1. Time series of ∑PNs, CH_3CN, Furfural, CO and pressure during the flight B623, shown as example.

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As described in the introduction, recently different compounds (CO, HCN or CH_3CN) and different concentrations thresholds have been introduced as tracers to establish if the air mass monitored is affected by forest fire emissions or not. These methods are summarized in Table 2.

Table 2. Methods to identify BB plumes.

	Methods
Holzinger et al. (2005)	$CH_3CN > 3\sigma$
Alvarado et al. (2010)	CO increase of at least 20 ppb respect to the background and its correlation with HCN or CH_3CN
Vay et al. (2011)	CO > 160 ppb, HCN > 500 ppt or CH_3CN > 225 ppt
Hornbrook et al. (2011)	CO > 175 ppb, HCN > 400 ppt, CH_3CN > 200 ppt
Tereszchuk et al. (2011)	HCN > 350 ppt
Lewis et al. (2013)	CO > 200 ppb and presence of furan or furfural
Palmer et al. (2013)	CO > 148 ppb, HCN > 122 ppt and CH_3CN > 150 ppt
Le Breton et al. (2013)	$HCN > 6\sigma$
This work	$\sum PNs > 6\sigma$ or $\sum PNs$ > 418 ppt

In our analysis we tested the use of the concentration profiles of ∑PNs as possible identifier of BB plumes. We applied two different methods: 1) evaluating the 99th percentile of the ∑PNs concentrations measured during the background flight B625 (as done by Palmer et al., 2013) and using this value as threshold to distinguish air masses emitted by fires; 2) applying the statistical approach (σ method). In the first case, we calculate the 99th percentile of the 1 second ∑PNs data sampled during the B625 finding a threshold of 418 ppt. In the second case, first we selected the parts of each flight identifiable as background and, then, we evaluated for these data the mean and the standard deviation of the ∑PNs; after that, we identified as BB plumes the parts of each flight in which the difference between ∑PNs concentrations and the background level were higher than 6 standard deviations of the background. This threshold has been evaluated calculating the correlation coefficients between the ∑PNs and the CO varying the sigma threshold between 10σ and 3σ for each flight in which the ∑PNs showed evident and clear plumes (such as B622 and B623): we found that the maximum R occurred when we selected the BB plume using the 6σ threshold. In Table 3 are summarized the correlation coefficients R and the percentage of flight selected as BB plume obtained for all the flights in analysis using both the methods just described. Moreover, we indicated the percentage of flight identified as BB plume applying all the methods listed in Table 2 to our dataset.

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Table 3. Correlation coefficient (R) and percentage (%) of each flight of the BORTAS campaign selected as BB plume using both the ∑PNs methods (6σ and 99th percentile thresholds) and percentage (%) of BB plume evaluated for each BORTAS flight using the methods applied in other studies.

Flight	**This study (∑PNs methods)**				**Other studies**		
	6σ		**∑PNs > 0.418** 99th percentile				
	R	*%*	*R*	*%*		*%*	*Comments*
B619a	-	0	-0.045	13.5	Palmer et al.	0	Only CO
					Vay et al.	0	Only CO
					Hornbrook et al.	0	Only CO
					Holzinger et al.	-	No CH_3CN
					Alvarado et al.	1.3	Only CO
					Lewis et al.	0	No Furfural – CO < 200
					Tereszchuk et al.	-	No HCN
					Le Breton et al.	-	No HCN
B619b	-	0	-0.168	1.3	Palmer et al.	0	Only CO
					Vay et al.	0	Only CO
					Hornbrook et al.	0	Only CO
					Holzinger et al.	-	No CH_3CN
					Alvarado et al.	0	Only CO
					Lewis et al.	0	No Furfural – CO < 200
					Tereszchuk et al.	-	No HCN
					Le Breton et al.	-	No HCN
B620	-	0	-	0	Palmer et al.	0	Only CO
					Vay et al.	0	Only CO
					Hornbrook et al.	0	Only CO
					Holzinger et al.	-	No CH_3CN
					Alvarado et al.	5.1	Only CO
					Lewis et al.	0	No Furfural - CO < 200
					Tereszchuk et al.	-	No HCN
					Le Breton et al.	-	No HCN

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B621a	0.953	59.1	0.951	77.6	Palmer et al.	58.9	
					Vay et al.	23.1	
					Hornbrook et al.	32.5	
					Holzinger et al.	72.3	
					Alvarado et al.	76.8	
					Lewis et al.	-	No Furfural – CO > 200
					Tereszchuk et al.	41.6	
					Le Breton et al.	47.7	
B621b	0.644	3.6	0.644	3.6	Palmer et al.	2.0	NO CH_3CN in the plume; missing data of HCN in the flight (only a plume)
					Vay et al.	0	NO CH_3CN in the plume; missing data of HCN in the flight (only a plume)
					Hornbrook et al.	0	NO CH_3CN in the plume; missing data of HCN in the flight (only a plume)
					Holzinger et al.	0.6	Missing data for the CH_3CN in the flight
					Alvarado et al.	14.4	
					Lewis et al.	-	No Furfural – CO >200
					Tereszchuk et al.	26.3	
					Le Breton et al.	32.4	Missing data (only a plume)
B622	0.867	51.9	0.864	55.8	Palmer et al.	52.2	
					Vay et al.	7.2	
					Hornbrook et al.	10.7	
					Holzinger et al.	50.0	
					Alvarado et al.	74.2	
					Lewis et al.	45.6	

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					Tereszchuk et al.	10.4	
					Le Breton et al.	51.1	
B623	0.804	41.2	0.776	42.6	Palmer et al.	76.9	No HCN
					Vay et al.	73.6	No HCN
					Hornbrook et al.	70.5	No HCN
					Holzinger et al.	80.5	
					Alvarado et al.	85.6	
					Lewis et al.	71.0	
					Tereszchuk et al.	-	No HCN
					Le Breton et al.	-	No HCN
B626a	-	0	-	0	Palmer et al.	0	No HCN
					Vay et al.	0	No HCN
					Hornbrook et al.	0	No HCN
					Holzinger et al.	0.6	
					Alvarado et al.	2.0	
					Lewis et al.	0	No Furfural – CO < 200
					Tereszchuk et al.	-	No HCN
					Le Breton et al.	-	No HCN
B626b	0.755	8.1	0.259	0.4	Palmer et al.	8.6	No CH_3CN
					Vay et al.	5.6	No CH_3CN
					Hornbrook et al.	3.7	No CH_3CN
					Holzinger et al.	-	No CH_3CN
					Alvarado et al.	8.5	
					Lewis et al.	1.9	
					Tereszchuk et al.	15.1	
					Le Breton et al.	19.3	
B627	-	0	0.073	11.0	Palmer et al.	0	No HCN
					Vay et al.	0	No HCN
					Hornbrook et al.	0	No HCN
					Holzinger et al.	0.3	
					Alvarado et al.	3.1	
					Lewis et al.	0	No Furfural – CO < 200
					Tereszchuk et al.	-	No HCN

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					Le Breton et al.	-	No HCN
B628a	-	0	-	0	Palmer et al.	0	
					Vay et al.	0	
					Hornbrook et al.	0	
					Holzinger et al.	0.3	
					Alvarado et al.	21.0	
					Lewis et al.	0	No Furfural – CO < 200
					Tereszchuk et al.	0	
					Le Breton et al.	40.1	
B628b	0.477	11.9	0.540	10.6	Palmer et al.	2.5	No HCN
					Vay et al.	0	No HCN
					Hornbrook et al.	0	No HCN
					Holzinger et al.	6.3	
					Alvarado et al.	61.1	
					Lewis et al.	0	No Furfural – CO < 200
					Tereszchuk et al.	-	No HCN
					Le Breton et al.	-	No HCN
B629	-0.036	6.4	-0.010	5.7	Palmer et al.	3.9	No HCN
					Vay et al.	1.1	No HCN
					Hornbrook et al.	0	No HCN
					Holzinger et al.	7.6	
					Alvarado et al.	6.2	
					Lewis et al.	0	No Furfural – CO < 200
					Tereszchuk et al.	-	No HCN
					Le Breton et al.	-	No HCN
B630	0.007	2.0	0.005	2.6	Palmer et al.	12.0	No HCN
					Vay et al.	5.1	No HCN
					Hornbrook et al.	2.4	No HCN
					Holzinger et al.	26.2	
					Alvarado et al.	42.9	
					Lewis et al.	-	No Furfural – peak with CO > 200
					Tereszchuk et al.	-	No HCN

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					Le Breton et al.	-	No HCN

In order to make the analysis as accurate as possible, the double flights were separated and applied all the methods in each part of the flights taking into account of different Canadian regions and different hours of the day during which we were flying. The ∑PNs methods give, in most cases, results in agreement with each of the methods that use CO, HCN and CH_3CN (see table 3) and allow to discriminate 3 flights (B621a, B622 and B623) in which a significant percentage (higher than the 40% with R ranging between 0.804 and 0.953) of the data have been collected sampling air masses emitted by biomass burning. Moreover, these results are also in agreement with what is found applying the approaches suggested in other studies. We found three flights (B621b, B626b and B628b) in which the majority of the methods show that a small percentage (less than 10% with R ranging between 0.477 and 0.755) of data can be identified as BB plumes (see table 3). In six flights (B619a, B619b, B620, B626a, B627 and B628a) the ∑PNs 6σ method suggests, in agreement with the majority of the other techniques, a dominance of background air masses sampled; the 99th percentile method applied to the ∑PNs for the flights B619a, B619b and B627 show a small fraction of flight selected as BB. Moreover, the R values between the ∑PNs and the CO in those points is so low (or even negative) to suggest that these parts of the flights are not ascribable as BB plume. The flights B629 and B630 present a small percentage of the flight identified as BB plume, using the ∑PNs methods (confirmed also by other methods), but the low (or negative) R values suggest a different origin for these plumes. Summarizing, we classified three flights (highlighted in grey in Table 3) with evidence of significant BB plumes sampled, three with a small percentage of BB plumes and 8 flights with a dominance of background air masses sampled. Le Breton et al. (2013) evaluated the percentage of flights ascribable as BB plumes using the 6σ method applied to their HCN measurements and the R^2 between the CO and the HCN in the BB plumes for five flights. Our results, with the percentage of flight identified as BB plume using their method, are in agreement with those that they presented, with the exception of the B621 flight. In this case, the difference could be due to the fact that we split the double flights into two datasets and also because for the B621b there are some missing data for the HCN and only one big plume. Moreover, the R^2 between HCN and CO range between 0.46 (B622) and 0.83 (B621) (Le Breton et al., 2013).

Figure 2 shows the scatter plot between the ∑PNs and the CO for the flights B621a, B622 and B623: the red circles are the BB plume selected by the 6σ of the ∑PNs technique and the green circles the background part of each flight

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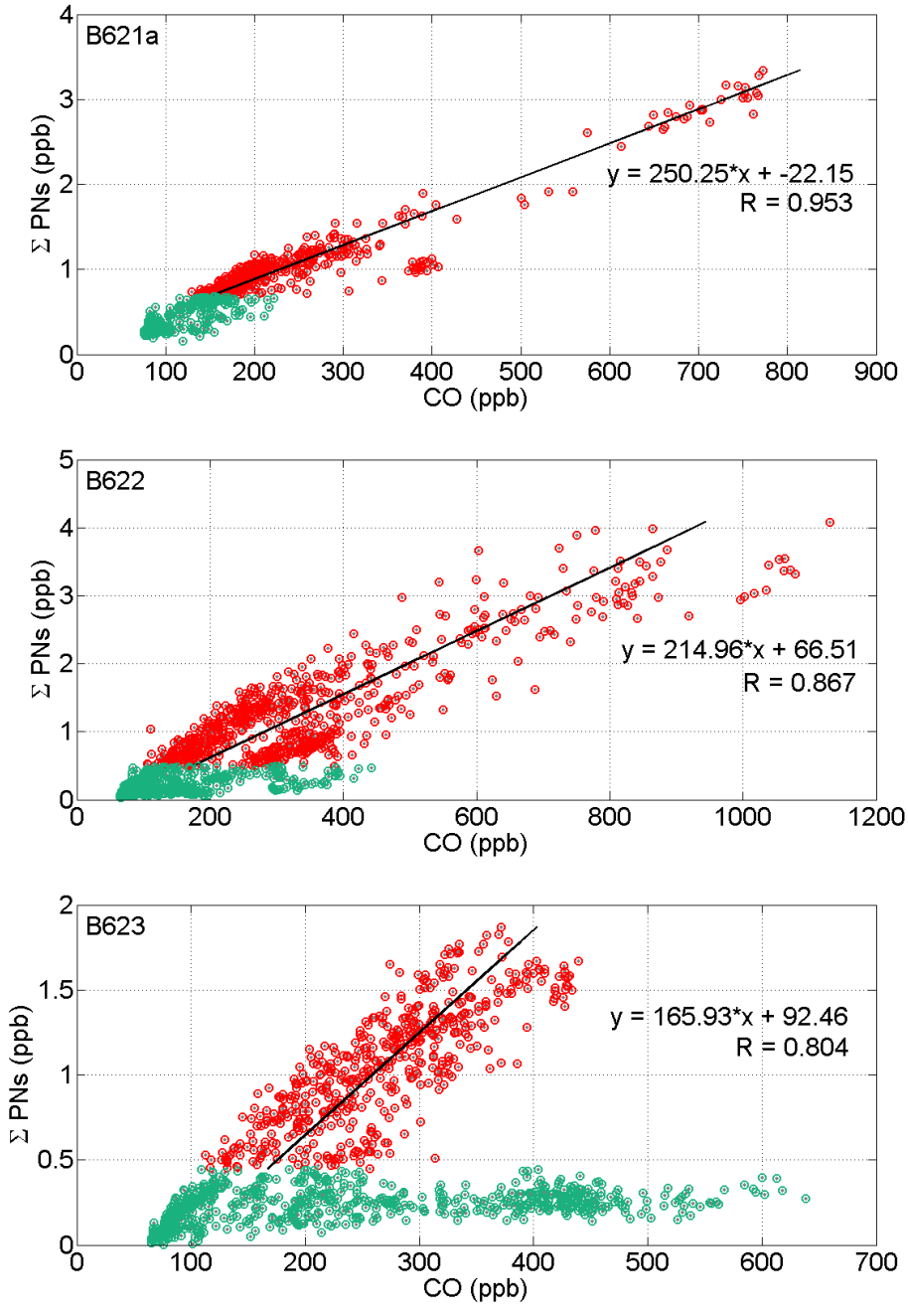

1 **Figure 2.** Scatter plot between the ∑PNs and the CO for the B621a, B622 and B623 flights (from the
2 top to the bottom, respectively). The red points indicate the data selected as BB plume using the 6σ
3 method to the ∑PNs measurements, the green points indicate the background air masses.

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The ∑PNs show a very good correlation with the CO, in presence of BB plumes: the correlation coefficients R, in fact, vary between 0.804 and 0.953. The data of the B623 flight (Figure 2) show an interesting, well distinct double trends between the ∑PNs and the CO; the time series (Figure 1) shows that the CO and the CH_3CN present two plumes (between $8.2x10^4$- $8.4\ x10^4$ seconds A.M. and between $8.6\ x10^4$-$8.8\ x10^4$ seconds A.M.) at pressure (P) higher than ~750 hPa (corresponding to an altitude of ~2000 m a.s.l.): at these plumes do not correspond an increase of the ∑PNs nor of the Furfural. In order to explain the double trends in the ∑PNs vs CO scatter plot of the flight B623 (see figure 2), we analysed the all dataset of this flight as function of the pressure, finding that the two trends can be distinguished using a pressure threshold of 750 hPa (Figure 3), or equivalently an altitude threshold of ~2000 m a.s.l. (not shown).

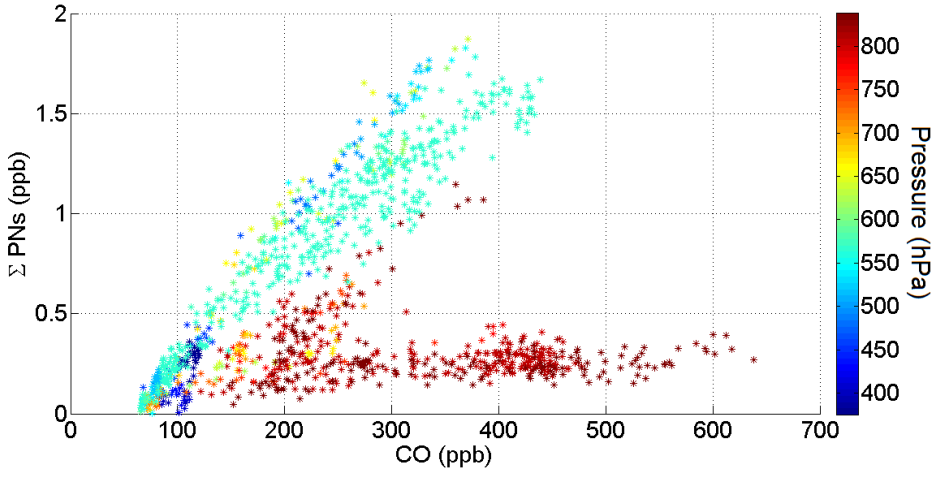

Figure 3. Scatter plot between the ∑PNs and the CO as function of the pressure of the flight B623.

The fact that the two distinct trends of the flight B623 are separable by the 6σ method of the ∑PNs and by pressure, suggests that the air masses sampled at different altitude are originated by different sources, and the smaller correlation (R = 0.31) between ∑PNs and CO for pressure above 750 hPa, supports the hypothesis that they are not impacted by BB emission. To prove this thesis, we evaluated the lagrangian back-trajectories (Hysplit model, Draxler et al., 1999) selecting the starting point at different altitudes along the flight trajectory and running the model up to 200 hours back. Panel c) in Figure 4 shows the black-trajectories of air masses sampled at pressure higher than 750 hPa (black points) or lower than 750 hPa (grey points): a different origin is clearly identifiable. In particular, air masses collected at lower altitudes (P > 750 hPa) come from the northern region of the Canada and the altitude of provenience increases the further back the trajectory goes and decreases in the last three days of simulation (Figure 4d); on the contrary the air masses corresponding to P < 750 hPa

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originated in the South-West region of the Canada (e.g., Alberta, Saskatchewan,…) and in the North-West states of the U.S.A. (e.g., Montana, Idaho, Wyoming, Washington, Oregon,…). Figure 4a represents the position of the air masses along the back-trajectories during the days between the July 12th and July 20th (corresponding respectively to -200 hours back and 0 hours back in the back-trajectories model setup). In the same way, Figure 4b shows the fire spots recorded by the FLAMBE (The Fire Locating And Monitoring of Burning Emissions, Reid et al., 2009) archives as function of the day in which the biomass burning occurred (between the July 11th and July 20th). The Figure 4 reveals not only that air masses collected for P > 750 hPa come from a different region of the North America respect to those collected for P < 750 hPa, but also that the regions of interest for air masses at P > 750 hPa are, most likely, not impacted by fire emissions, at least for the days in which the air masses passed over those areas. On the contrary, the plumes (identified as BB plumes) measured at P < 750 hPa (i.e. altitude higher than 2000 m a.s.l.) have originated from regions strongly influenced by biomass burning fires (see panel b of figure 4) in the central-west coast of the North America) in the days of July in which the air masses flew above those territories. The back-trajectories analysis, therefore, confirm the existence of two different layers of air masses sampled during the B623 flight distinguishable by the pressure (i.e. the altitude).

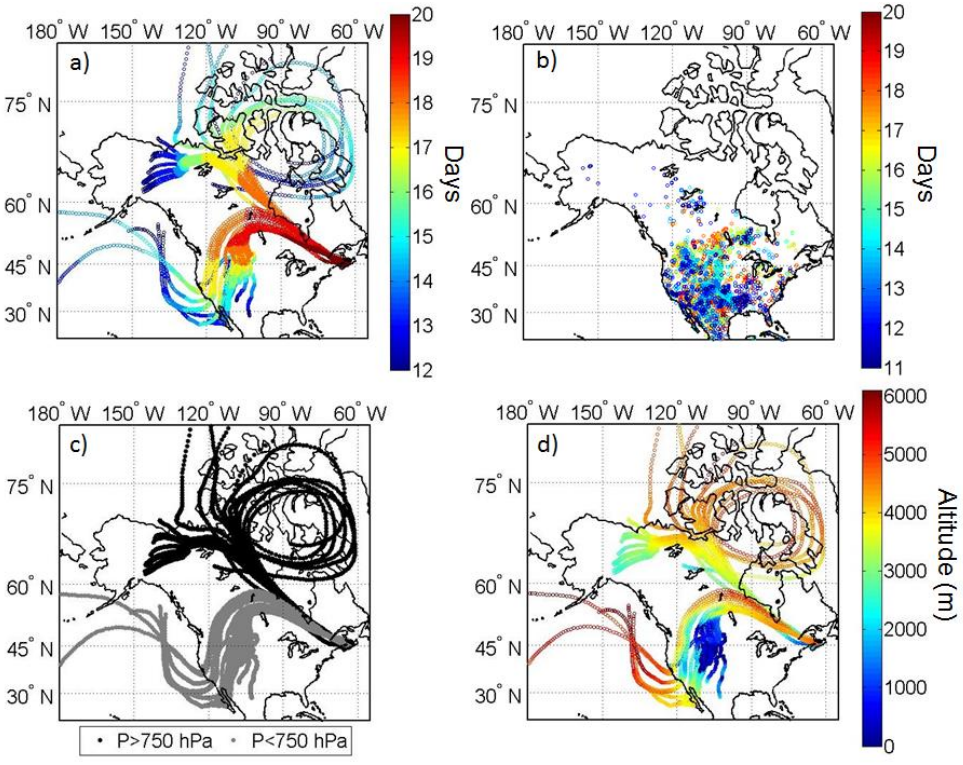

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Figure 4. Panel a): temporal position (express as day from the 12th July to the 20th of July) along the 200 hours back-trajectories. Panel b): spot of the biomass burning fires derived from the FLAMBE archive as function of the day in which they occurred (from 11th July to 20th July – we selected the dataset at the 13.00 UTC and the 23.00 UTC). Panel c): distinction of the back trajectories position selecting the starting point along the flight trajectories for $P \gtrless 750\ hPa$. Panel d): altitude along the back trajectories.

Finally, we evaluated the qualitative age of the air masses sampled during the B623 flight: using the ratio between the NO_x (sum of the TD-LIF NO_2 and the chemiluminescence NO measurements) and the total NO_y (measured by the TD-LIF and the calculated as sum of NO_x and its oxidation products), we observed that the air masses sampled at P < 750 hPa are younger respect those sampled at higher pressure confirming that the air masses identifiable by the pressure are distinct not only for their sources (and provenience), but also for the age.

Considering what has been highlighted analysing the double trends in the CO vs ∑PNs plot of the B623, we examined in depth the correlation between the CO and the ∑PNs for all the flights and we found that also other flights show similar trends: in fact, B621a and the B622 show two different trends that can be distinguished using a pressure threshold of 700 hPa (figure not shown). Moreover, we did the same analysis also for the HCN: we found that for the B621a, B622 the scatter plot (plotting only the data selected as BB plume using the Le Breton et al. (2013) method) between the HCN and the CO shows different trends that can be distinct by the pressure (Figure 5, panel a and b related to the B621a and B622 flight, respectively). This analysis suggest that, even though the identification of a BB plume done using different chemical species threshold is largely and successfully employed (Le Breton et al., 2013; Lewis et al., 2013; Palmer et al., 2013; O'Shea et al. 2013), there are some episodes in which the introduction of other parameters (such as the pressure or the altitude, which are indicative of the vertical position of the air masses and, therefore, may be particularly significant for observations on-board aircrafts) gives interesting information and allow to discriminate better and with more details the plumes. The back-trajectories evaluation also gives an important indication of the origin of the air masses and completes the analysis.

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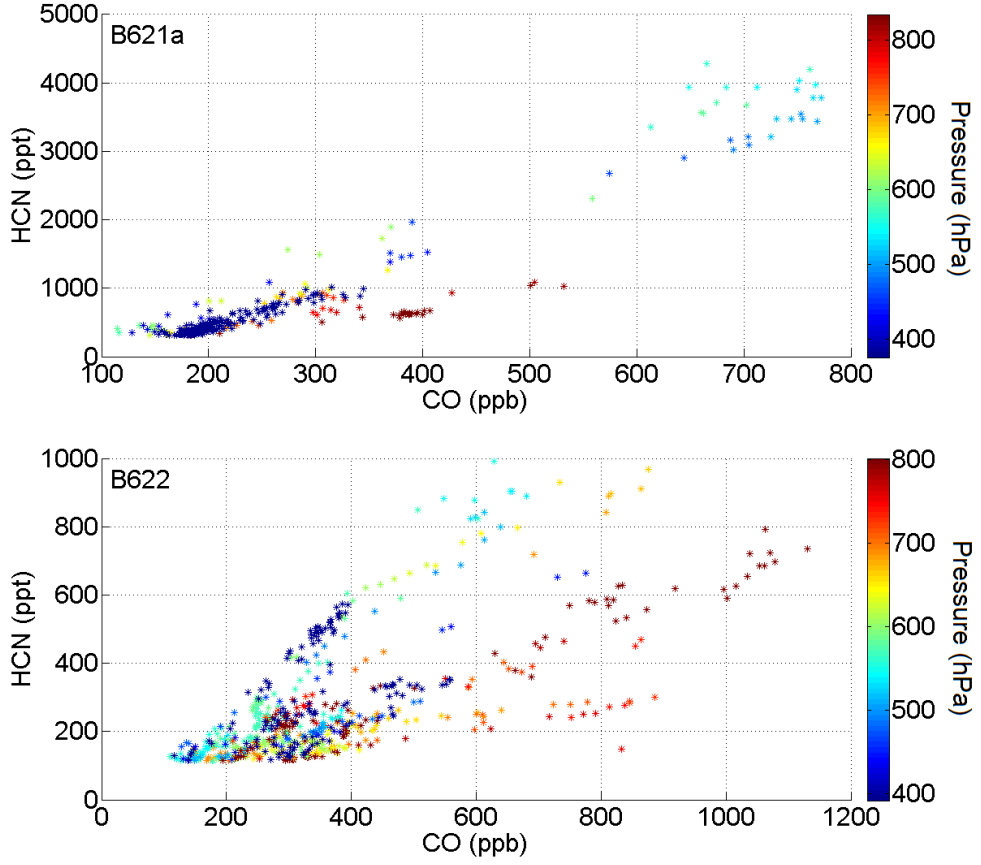

Figure 5. Scatter plot between the HCN and the CO as function of the pressure for the flights B621a (at the top) and B622 (at the bottom).

4. Model results

In order to refine the methods to discriminate the BB plumes and better understand the origin of the air masses analysed in the BORTAS campaign, an artificial neural network (ANN) model, recently developed for O_3 and PM studies (Biancofiore et al., 2015a; Biancofiore et al., 2015b), has been adapted and used with BORTAS dataset. The ANN is capable of simulating non-linear relationships (Lonbladd et al. 1992) and for this reason is ideal for investigating the relationship between ∑PNs (and HCN) and chemical and physical parameters. In this work, a recurrent architecture was used (Elman, 1990) that provides a multi-step memory. We simulated the concentrations of the ∑PNs for the B623 flight and of the ∑PNs and the HCN for the B622. During both these flights the scatter plots between the ∑PNs and the CO or the HCN and the CO show different trends that we distinguished by the pressure and that are indicative of air masses having different origins (coming from regions

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interested by fires or not), as explained in Section 3. We carried out two different simulations: a) we used as input for the neural network only the O_3, CO, NO and CH_3CN (case A); b) we used as input the O_3, CO, NO, CH_3CN and the pressure (case B). In this way, we evaluated if and how the simulations of the ∑PNs and the HCN change by adding a physical parameter to the inputs, therefore taking into account the position of the air masses (that is the altitude of the aircraft during the flights). Figure 6 shows the results of the case A simulations for the flight B622: the scatter plot between the simulated HCN (panel a) and ∑PNs (panel b) and the measured CO as function of the pressure does not present distinct trends as evident in the measured data. Similar results have been found for the case A simulations (panel c in Figure 6) of the flight B623: the net separation of two trends in the ∑PNs vs CO scatter plot of the measured data (Figure 2) is not reproduced by the model. On the contrary, adding the pressure to the inputs (case B) the simulations improve significantly for both the flights and both the species; Figure 7 shows the ANN simulations in the case B. It is evident that the different trends, identifiable by the pressure using the measured data (Figure 3 and Figure 5), are well reproduced and become evident despite what occurred in the case A (Figure 6). Moreover, it is clear also that the correlation coefficients between the ∑PNs measured and the ∑PNs simulated increase adding the pressure to the inputs (these results are highlighted in grey in Table 4): in fact, R improves from 0.94 (case A) to 0.95 (case B) for the B622 flight and, even more, from 0.77 (case A) to 0.94 (case B) for the flight B623, in which the two trends between the ∑PNs and the CO is significantly more evident respect to the B622 flight. Similar results can be found for the HCN: the correlation coefficient R, in fact, increases from 0.86 (case A) to 0.92 (case B). In addition to the correlation coefficient R, we estimated the model performances using three more typical indices (Biancofiore et al., 2015): the fractional bias (FB), the normalized mean squared error (NMSE) and the factor of 2 (FA2). The results are summarized in Table 4. The FB is calculated as the ratio between the difference of the mean observed and the mean modelled concentrations and their mean; it indicates the systemic errors that can entail a bias between the modelled and the measured data and can range between -2 (overestimation) and +2 (underestimation): an ideal model has an FB index of 0. The NMSE is the result of the ratio between the mean of the squared difference between the observed and the modelled concentrations and the sum of their mean; it gives information about the total errors of the models and the best value is 0 (as the NMSE decreases approaching 0, the model performance increases). Finally, the FA2 is the percentage of the simulated data for which the ratio between the observed and the modelled concentrations is included between 0.5 and 2; the ideal model has an FA2 of 1 and the worst results occur if FA2 is equal to 0. The ∑PNs simulation for the flight B622 shows that R, NMSE and the FA2 improve adding the pressure to the inputs (case B); on the contrary, the FB results slightly worst indicating that the model tends to overestimate the concentrations. The HCN simulation for the

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flight B622 has better results for all the indices with the exception, also in this case, of the FB which is lightly greater in the case B than in the case A. Finally, the R, FB and FA2 of the ∑PNs modelled for the flight B623 show a significant improvement in the case B respect the case A, but the NMSE presents a worsening suggesting the possibility of an increase in the systemic or random errors.

Table 4. Indices to evaluate the Model performances. R is the correlation coefficient, FB is the fractional bias, NMSE is the normalized mean squared error and FA2 the factor of 2. See the text for a description of these indices

	Simulations	R	FB	NMSE	FA2
∑PNs (B622)	Case A	0.94	-0.017	0.124	0.755
	Case B	0.95	-0.023	0.099	0.763
HCN (B622)	Case A	0.86	0.009	0.228	0.946
	Case B	0.92	0.014	0.136	0.959
∑PNs (B623)	Case A	0.77	0.014	0.028	0.771
	Case B	0.94	-8.8e-4	0.079	0.867

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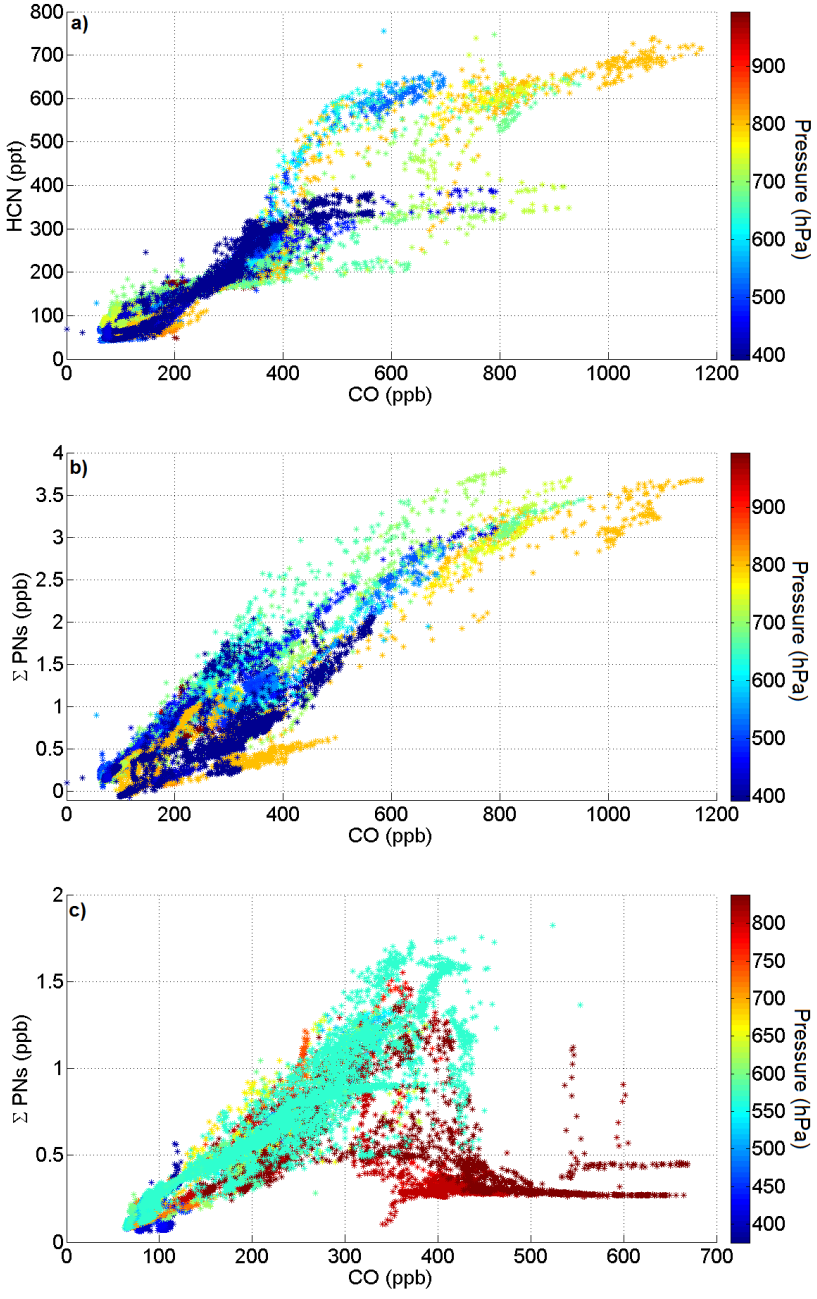

Figure 6. Simulations results for the case A (only O_3, CO, NO and CH_3CN as inputs): scatter plot between the simulated HCN (panel a)), the simulated ∑PNs (panel b)) and the CO for the B622 and between the simulated ∑PNs and CO for the B622 (panel a)) and the B623 (panel b)).

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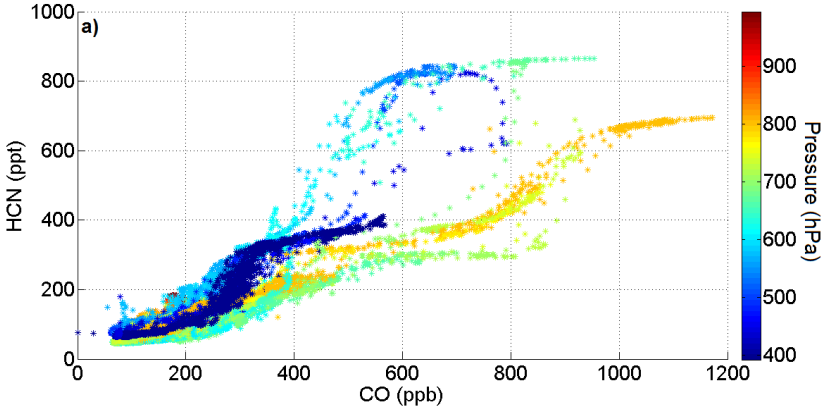

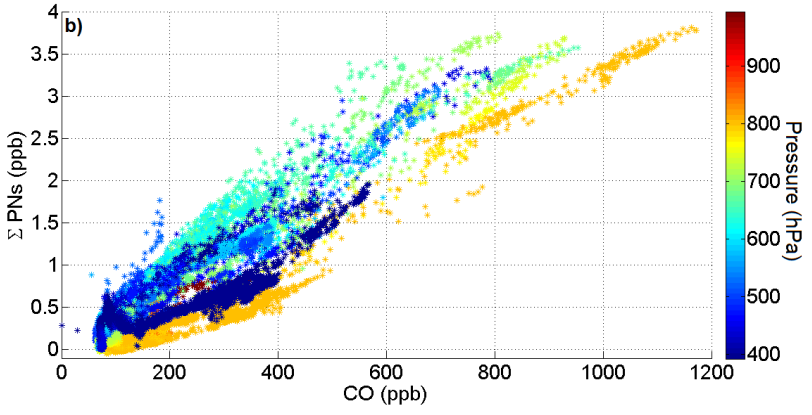

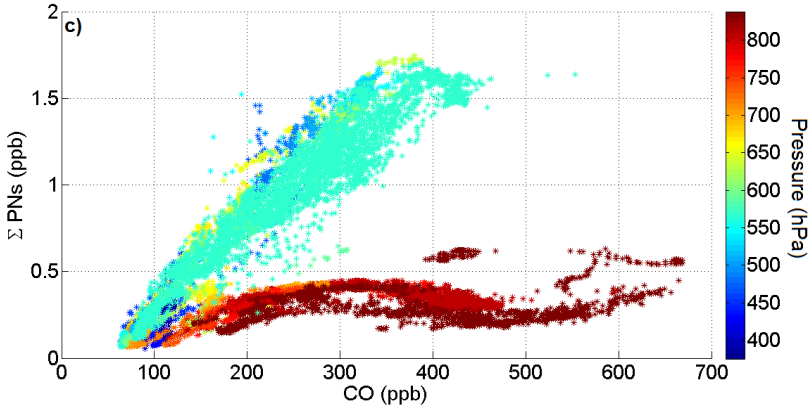

Figure 7. Simulations results for the case B (O_3, CO, NO, CH_3CN and pressure as inputs): scatter plot between the HCN (panel a)) simulated and the CO for the B622 and between ∑PNs and CO for the B623 (panel b)).

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Conclusions

The measured ∑PNs during the BORTAS aircraft campaign show a good correlation (R varying between ~0.80 and ~0.95) with CO for different flights. We used ∑PNs as BB tracers applying two different methods to select a BB plumes: 1) we defined a threshold of 6σ of ∑PNs concentration for each flights and all the data that are 6σ times higher than the background level have been selected as BB plume; 2) evaluating the 99th percentile of the ∑PNs measurements done during the B625 flight (considered a background flight not affected by BB plumes). Moreover, we applied several methods present in the literature to our dataset to compare with the proposed ∑PNs methods and we calculated the percentage of flight classifiable as BB plume; we found that all the methods identified four flights with evident and significant percentage of BB plumes intercepted. Therefore for most of the flights the ∑PNs methods can be an alternative to identify BB. Moreover, we found that in some flights the scatter plot between the ∑PNs and the CO (or the HCN and the CO) shows different slopes identifiable by a pressure threshold, suggesting different regimes between these species that is different air masses. The dependency of these slopes by the pressure suggested that the air masses sampled could be spatially (vertically) different and that their origins could be different. Analysing the back-trajectories, as expected, we found that the air masses were not all originated by biomass burning and that those at lower pressure (i.e. higher altitude) reach Nova Scotia from the clean northern region of the Canada. In order to refine the method we adapted an ANN model simulating the ∑PNs and the HCN in two different ways: 1) using only the CO, NO and CH_3CN as inputs; 2) adding also the pressure to the inputs. We found that the model results improve in the second case. In conclusion, we suggest that the ∑PNs can be used as BB tracer for the identification of BB plumes; moreover, as consequence of the ∑PNs vs CO analysis and of the model results, we suggest that the use of a meteorological parameter (such as pressure) could allow a better discrimination of the air masses origin and a more selective method for the selection of BB plumes.

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